566

Influence of Ionic Force on the Instability Constants of
Halogen and Pseudo-Halogen Complex Compounds. (Cont.)
the Davies[9] equation can similarly be used for converting
the constant to zero ionic force if this latter is below
values of the order of 0.8. The instability constant for
the $ZnCNS^+$ complex has also been found by the equilibrium-
shift method in the system Fe^{3+} − CNS^- electrolyte.

There are twenty five references, four of them Russian.

Ref.9 is C.W.Davies, J.Amer. Chem. Soc., 2093, (1938).

5 Tables, 5 Figures, 19 Equations.

Ivanovskiy Chemical Technology Institute,
Received 11 September, 1956.

Card 2/2

1. Ivanovskiy Khimiko-Tekh. Inst.

VATSMIRSKIV, K.B

Effect of ...

YATSIMIRSKIY, K. B.

78-3-2/35

AUTHOR: Yatsimirskiy, K. B.

TITLE: Thermodynamics of Complex-Formation Reactions
in Solutions.   (Termodinamika Reaktsiy
Kompleksoobrazovaniya v Rastvorakh).

PERIODICAL: Zhurnal Neorganicheskoy Khimii, 1957, Vol.II,
Nr.3, pp. 491-501.   (USSR)

ABSTRACT: This is a report presented at the Seventh All-Union
Conference on the chemistry of complex compounds,
held 12th October, 1956.   Starting from a brief review
of methods used recently for the investigation of
equilibria in solutions of complex compounds, the author
goes on to show in a tabular form the relative amount of
effort devoted to the study of the stability of various
complex compounds in solution. • Attention is drawn to
the importance of the question as to whether all inter-
mediate steps are realised in step-wise complex formation.
This question is fundamental to the mathematical methods
used for treating experimental data and for the relation-
ships between the stepwise instability constants.   It is

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.Thermodynamics of Complex-Formation Reactions in Solutions.

shown that best agreement between experimental and
calculated data for aluminiumfluoride complexes was
obtained with the use of the equation proposed by Van
Panthaleon[13]; this equation also gives good results
for other fluoride complex compounds and also for several
complexes with ammonia, imidazole and other substances.
The data presented show that careful study must be made
not only of the composition of the intermediate complex
particles, but also of their stereochemical features.
Thermodynamic functions for step-wise complex formation
are tabulated for different series of compounds, and a
table is also presented showing the distribution of
electrons by energy levels in an octahedral field. It
is shown that the ideas used can lead to explanations of
observed regularities in the changes of the stability of
complex compounds and also of apparent discrepancies.
There are 11 figures, 5 tables and 27 references, 10
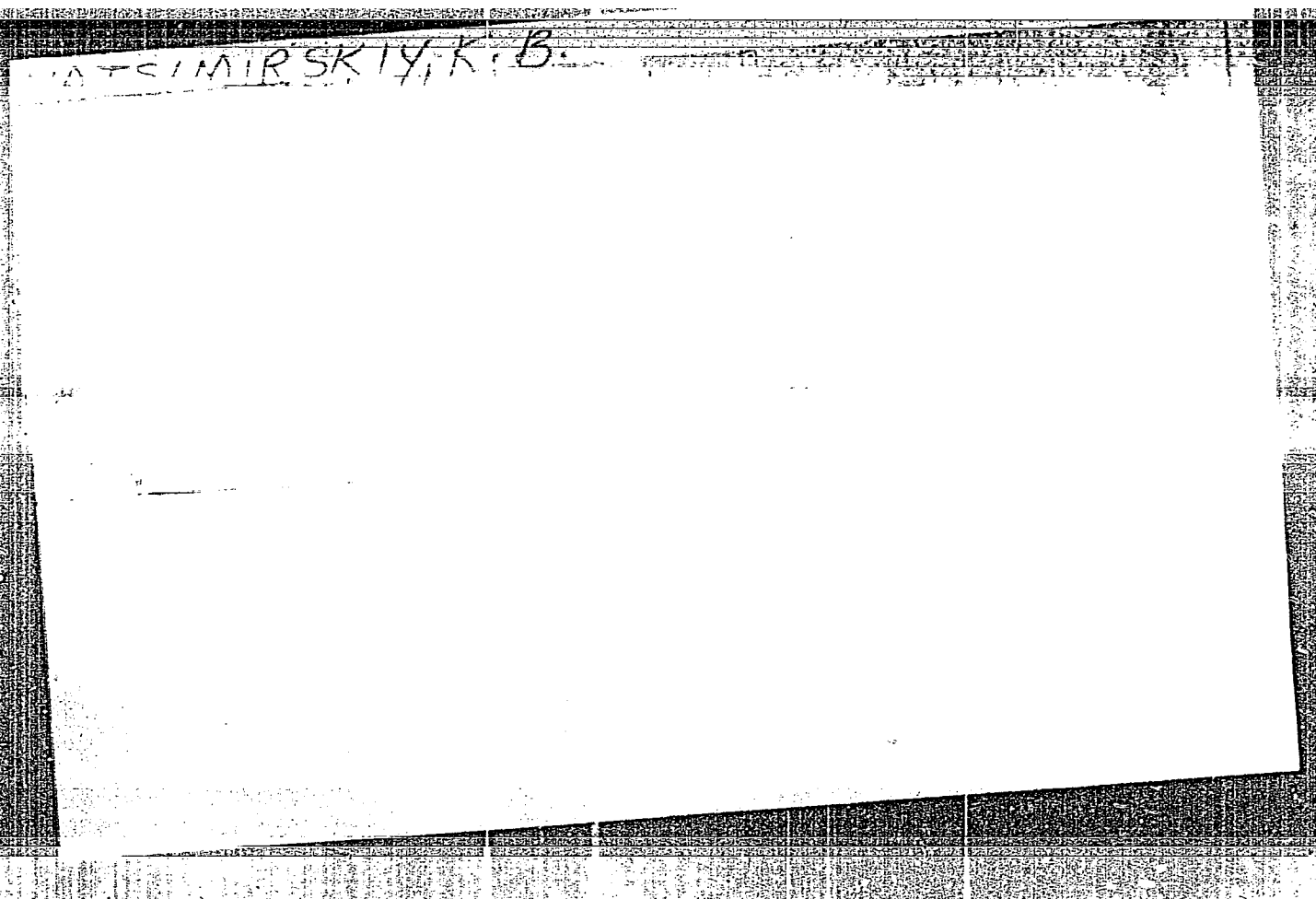of which are Slavic.

SUBMITTED: 29 October, 1956.
Card 2/2

YATSIMIRSKIY, K.B.

YATSIMIRSKIY, K.B.; GUS'KOVA, L.V.

Thermochemistry of thiosulfate complexes of cadmium and zinc.
Zhur.neorg.khim. 2 no.9:2039-2042 S '57.   (MIRA 10:12)

1.Ivanovskiy khimiko-tekhnologicheskiy institut im. D.I. Mendeleyeva.
          (Thermochemistry) (Cadmium thiosulfate)
          (Zinc thiosulfate)

ATSIMIRSKIY, K. B.

YATSIMIRSKIY, K.B.

The entropy of polyatomic ions [with summary in English]. Zhur.
fiz.khim. 31 no.9:2121-2126 S '57.   (MIRA 11:1)

1.Khimiko-tekhnologicheskiy institut, g. Ivanovo.
            (Entropy) (Ions)

YATSiMiRSKIY, K.B.

YATSIMIRSKIY, K. B.

SOV/1900

PHASE I BOOK EXPLOITATION

Akademiya nauk SSSR.   Komissiya po analiticheskoy khimii

Primeneniye radioaktivnykh izotopov v analiticheskoy khimii (Use of Radioactive Isotopes in Analytical Chemistry) Moscow, Izd-vo An SSSR, 1958. 366 p. [Series: Its: Trudy, t. 9 (12)] Errata slip inserted. 3,000 copies printed.

Resp. Ed.: I.P. Alimarin, Corresponding Member, USSR Academy of Sciences; Ed. of Publishing House: A.M. Yermakov; Tech. Ed.: E.V. Polyakova.

PURPOSE: The book is intended for chemists and chemical engineers concerned with work in analytical chemistry.

COVERAGE: The book is a collection of the principal papers presented in Moscow at the Second Conference on the Use of Radioactive Isotopes. The problems discussed are solubility limits, determination of the instability constants of complex compounds, separation of rare earth metals, and ion-exchange chromatography. No personalities are mentioned. There are 351 references, 175 of which are Soviet, 33 German, 19 French, 8 Swedish, 2 Bulgarian, and 2 Czech.

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153 -58-1-8/29

AUTHORS: Yatsimirskiy, K.B., Alekseyeva, I.I.

TITLE: The Investigation of Absorption Spectra and the Determination of the Dissociation Constants of Molybdic Acid (Izucheniye spektrov pogloshcheniya i opredeleniya konstant dissotsiatsii molibdenovoy kisloty)

ABSTRACT: A process of depolymerization is assumed to take place during the dilution of molybdic acid solutions, and it is believed that highly diluted solutions contain nearly only monomeric particles. The correctness of this assumption is confirmed also by the study of complex molybdenum compounds (by the application of the kinetic method). The authors were therefore interested in investigating these diluted molybdic acid solutions by the optical method. They obtained the following results: Highly diluted molybdic acid solutions contain no polymerized particles, which proves the constancy of the molar extinguishing coefficient within a fairly extensive interval of the molybdenum concentrates ($2 \cdot 10^{-5}$ to $2 \cdot 10^{-4}$ M). By the kinetic method it was established that in acid solutions and

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The Investigation of Absorption Spectra and the Determination
of the Dissociation Constants of Molybdic Acid   153-58-1-8/29

in the case of a high degree of dilution mainly non-dissociated
molecules of molybdic acid exist. It may therefore be expected
that in the case of low pH-values non-dissociated molecules, but
at higher pH-values hydromolybdate- and molybdate ions will be
found (as dissociation products of molybdic acid). For the de-
termination of the H_2MoO_4-dissociation constants and for the pur-
pose of investigating the absorption spectra the dependence of
the optical density of the solutions upon the concentration of
the hydrogen ions was studied. According to the course taken by
the curve (fig.1) the existence of 3 kinds of particles with
diverse molar extinguishing coefficients according to pH values
must be expected. On the strength of the experimental data ob-
tained absorption spectra of molybdic acid as well as of dissoci-
ation products were obtained (fig.3). There are 3 figures, 3
tables, and 6 references, 2 of which are Soviet.

ASSOCIATION: Kafedra analiticheskoy khimii (Chair of Analytical
               Chemistry)

SUBMITTED: September 10, 1957

Card 2/2

5(2)

AUTHORS: Yasinskene, E. I., Yatsimirskiy, K. B.   SOV/153-58-2-6/30

TITLE: Examination of the Complex Compounds of Iron (III) and
             Titanium (III) With Urea (Issledovaniye kompleksnykh
             soyedineniy zheleza (III) i titana (III) s mochevinoy)

PERIODICAL: Izvestiya vysshikh uchebnykh zavedeniy. Khimiya i khimicheskaya
             tekhnologiya, 1958, Nr 2, pp 31-35 (USSR)

ABSTRACT: When mixing a diluted iron (III) nitrate solution with urea
             there is no perceptible change of color. This prevents a
             direct examination of such systems by measuring the optical
             density of solutions with different urea concentrations. On the
             other hand, it has been stated that the color intensity of
             solutions of the iron rhodanide complexes decreases more
             distinctly by an addition of urea solution than by a dilution
             with equal quantities of water. This could only be explained by
             the formation of an iron urea compound. Therefore, the
             iron (III) compounds with urea have been studied by means of
             decolorizing the solutions which contain iron rhodanide
             complexes. A literature survey on the latter is given (Refs 1-6).

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Examination of the Complex Compounds of Iron (III)   SOV/153-58-2-6/30
and Titanium (III) With Urea

From this, it has become obvious that it is possible to make a
solution in which the complex $FeSCN^{2+}$ will be predominantly
present. For their calculations, the authors required a
knowledge of the instability constant of the iron (III)
rhodanide complex $K_{FeSCN^{2+}}$.

C o n c l u s i o n s :   The authors have studied the system
$Fe^{3+}-SCN^- -CON_2H_4$ by means of the optical method. They
determined the formation of complex compounds in the solution:
$FeCON_2H_4^{3+}$ and $Fe(CON_2H_4)_2^{3+}$. The instability constants of
these complexes were determined as 1.01 and 2.00, respectively;
the ionic strength being 0.103 and the temperature 18-20° .
2) Urea-containing, diluted, acid $TiCl_3$-solutions have been
studied. The formation of a complex compound $Ti(CON_2H_4)^{3+}$ in
the solution was determined; its instability constant at the
ionic strength 0.261 and at 18-20° was k = 2.69 .

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Examination of the Complex Compounds of Iron (III)   SOV/153-58-2-6/30
and Titanium (III) With Urea

There are 4 figures, 2 tables, and 11 references, 5 of which
are Soviet.

ASSOCIATION: Vil'nyusskiy gosudarstvennyy universitet im. V. Kapsukasa i
Ivanovskiy khimiko-tekhnologicheskiy institut
(Vilnyus State University imeni V. Kapsukas and Ivanovo
Chemical-Technological Institute)
Kafedra analiticheskoy khimii
(Chair of Analytical Chemistry)

SUBMITTED: September 10, 1957

Card 3/3

5(2)
AUTHORS: Yatsimirskiy, K. B., Berezin, B. D.   SOV/153-58-2-8/30

TITLE: The Indicators of Mercurimetry (Indikatory merkurimetrii)
              Communication I. Sodium Nitroprusside (Soobshcheniye I.
              Nitroprussid natriya)

PERIODICAL: Izvestiya vysshikh uchebnykh zavedeniy. Khimiya i khimiches-
              kaya tekhnologiya, 1958, Nr 2, pp 43 - 50 (USSR)

ABSTRACT: The method of mercurimetric analysis is used at
              present in the determination of various substances
              on a large scale. It is based on the capability
              of the ions of bivalent mercury of forming stable
              complex compounds with several anions and molecules
              according to the reaction
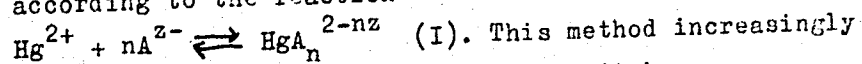
              $Hg^{2+} + nA^{z-} \rightleftharpoons HgA_n^{2-nz}$ (I). This method increasingly

              replaces the argentometric method, as it has a
              number of advantages over the latter. The mercurimetric
              method is, however, hardly known in quantitative
Card 1/4   respect. The limits of its applicability with various

The Indicators of Mercurimetry. Communication I.   SOV/153-58-2-8/30
Sodium Nitroprusside

indicators as well as the most important quantitative
characteristics of the latter are not known. The
present paper deals first of all with the investigation
of the solubility of $Hg[Fe(CN)_5NO]$. In the experimental
part first the solubility of this indicator is
studied in water. Table 1 gives the results. Further-
more its solubility is investigated by the pre-
cipitation method (Table 2). From the data of
table 1 the authors attempted to calculate the
solubility product $+ k^s_{HgNpr}$ of mercury nitroprusside
from the following relation: $K^s_{HgNpr} = [Hg^{2+}][Npr^{2-}] (1)$.

From the observation of the process of stepwise
complex formation (IV) the expression of the correction
for the stepwise complex formation is determined. After
this correction is introduced, and after the
simplification and insertion of known quantities, the
following equation is obtained:

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The Indicators of Mercurimetry. Communication I.   SOV/153-58-2-8/30

Sodium Nitroprusside

$$\Delta V_{ml} = 2.64 \cdot 10^{-5} \cdot \frac{V_{end}}{c^0_{Hg^{2+}}} \cdot \sqrt{\frac{[HgCl_2]}{[Npr^{2-}]}} \quad (5)$$

where ΔV_{ml} denotes the correction (in ml) of the titration liquid mercury nitrate of a concentration $c^0_{Hg^{2+}}$; it is always detracted from the final volume of the mercury nitrate solution used for the titration; V_{end} denotes the final volume of the solution after the titration; $[HgCl_2]$ and $[Npr^{2-}]$ denote the concentrations of mercuric chloride or nitroprusside, respectively in the solution after the titration. To prove that the equation (5) fully reflects the nature of the correction in the mercurimetric determination of the chloric with the nitroprusside indicator under normal titration conditions table 4 gives a comparison of the corrections calculated according to (5) with those experimentally found. The experimental data

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The Indicators of Mercurimetry. Communication I.   SOV/153-53-2-8/30
Sodium Nitroprusside

of table 4 permit the conclusion that the equation (5) can be used for a sufficiently accurate calculation of the mentioned corrections if the titration is carried out fairly slowly and under constant stirring (by hand). These possibilities make sodium nitroprusside one of the best indicators of mercurimetry. There are 1 figure, 4 tables, and 13 references, 4 of which are Soviet.

ASSOCIATION: Ivanovskiy khimiko-tekhnologicheskiy institut (Ivanovo Chemical Technological Institute) Kafedra analiticheskoy khimii (Chair of Analytical Chemistry)

SUBMITTED: September 10, 1957

Card 4/4

5(4), 5(2)
AUTHORS: Yatsimirskiy, K. B., Fedorova, T. I.   SOV/153-58-3-7/30

TITLE: Investigation of Formate and Thiocyanate Complexes
                of Bivalent Chromium (Izucheniye formiatnykh i
                rodanidnykh kompleksov dvukhvalentnogo khroma)

PERIODICAL: Izvestiya vysshikh uchebnykh zavedeniy. Khimiya i khimiches-
                kaya tekhnologiya, 1958, Nr 3, pp 4o - 45 (USSR)

ABSTRACT: In continuation of the papers hitherto published
                (Ref 1) the authors decided to study the composition
                and stability of the complexes under review. The
                measurements of the optical density were carried
                out by means of the photometer FM'. Titrated
                solutions of chromium (II) chloride, sodium formate
                and potassium thiocyanate were used for that purpose.
                Preliminary experiments already demonstrated a
                variation of the color and its intensity, respectively,
                in pouring together the first and second (Refs 2-4),
                and the first and third solution, respectively.
Card 1/3   For the investigation of the complex chromium (II)

Investigation of Formate and Thiocyanate Complexes of   SOV/153-58-3-7/30
Bivalent Chromium

compounds with formate by the optical method light
absorption curves of chromium (II) chloride
without and with formate were plotted (Fig 1). The com-
position and stability of the complex compounds
formed were determined by mixing the chromium
chloride solutions (with a constant concentration
0.47 mols/ℓ) with sodium formate solutions of
variable concentration (from 0.05 to 10 mols/ℓ).
The optical density of these solutions was then
determined by means of a light filter (transmission
range at 618mμ). The results are presented in table 1
and figure 2. The chromium thiocyanate complexes
were studied with two light filters: 619 and 574 mμ.
The results (for λ = 574 mμ) are given in table 3 and
figure 2. It was proved by these investigations
that bivalent chromium forms with formate and
thiocyanate in solutions complex compounds of the
following composition: $CrHCOO_a^+$, $Cr(HCOO)_2$, $CrCNS_a^+$,
$Cr(CNS)_2$. The instability constants of these complexes

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Investigation of Formate and Thiocyanate Complexes of   SO7/153-58-3-7/36
Bivalent Chromium

at 25° and at a ionic strength = 0 were calculated
and are given. There are 6 figures, 4 tables, and 7
references, 4 of which are Soviet.

ASSOCIATION: Ivanovskiy khimiko-tekhnologicheskiy institut (Ivanovo
Institute of Chemical Technology) Kafedra analiticheskoy
khimii (Chair of Analytical Chemistry)

SUBMITTED: September 10, 1957

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SOV/153-58-3-29/30

5(4)
AUTHOR: Yatsimirskiy, K. B.

TITLE: Calculation of the Stabilization Energy on a Splitting of the
              Main Level in the Crystalline Field (Raschet energii
              stabilizatsii za schet rasshchepleniya osnovnogo urovnya v
              kristallicheskom pole)

PERIODICAL: Izvestiya vysshikh uchebnykh zavedeniy. Khimiya i
              khimicheskaya tekhnologiya, 1958, Nr 3, pp 170-172 (USSR)

ABSTRACT: On the action of the crystalline field on an ion with ex-
              ternal d-electrons the main energy level is split up into sev-
              eral new ones. The electron redistribution to these levels is
              accompanied by an increase in energy Δ (Ref 1 - only for spe-
              cial cases). The author tries to find a general solution of
              the problem of the calculation of Δ. After various steps he
              arrives at the general equation for the calculation of the in-
              crease in energy due to the action of the crystalline field on
              an ion with d-electrons:

$$\Delta = \Sigma \left(\frac{N}{5} \nu_i - n_i'\right)(E_i - E_1) \qquad (6),$$

              where $\frac{N}{5}$ denotes the average electron number for one cell,

Card 1/3

Calculation of the Stabilization Energy on a Splitting of the Main Level in
the Crystalline Field

ν_1, ν_2 ....ν_m the number of cells for each level, n_1, n_2 ...n_i,
n_m the electron number in these cells, and E_1, E_2 ...E_m the
energies of the newly formed levels. The author discusses some
special cases: octahedral field, tetrahedral and tetragonal
field, and derives the corresponding equation for each of
them. Among the tetragonal field two extreme cases were dealt
with: a) The tetragonal bipyramid represents an only slightly
deformed octahedron, and b) The tetragonal bipyramid is
maximally expanded along the axis of the fourth order. In the
table the values of the multiplier before $(E_4 - E_1)$ as well as
those before $(E_2 - E_1)$ in the equations (7a), (8), and (12) are
mentioned for the series of ions with two charges. The data
mentioned show that the position of the stability maximum due
to the action of the crystalline field depends on the spatial
arrangement of the surrounding particles: in an octahedral
surrounding the maximum decreases to V^{2+} and Ni^{2+}, and in a
tetragonal one to Ti^{2+} and Co^{2+}. The author had arrived at the

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Calculation of the Stabilization Energy on a Splitting of the Main Level in
the Crystalline Field

SOV/153-58-3-29/30

same conclusions, now proved by experimental results, already
at some earlier time on the basis of other considerations
(Ref 3). There are 1 table and 3 references, 1 of which is
Soviet.

ASSOCIATION: Ivanovskiy khimiko-tekhnologicheskiy institut (Ivanovo Insti-
tute of Chemical Technology) Kafedra analiticheskoy khimii
(Chair of Analytical Chemistry)

SUBMITTED: January 18, 1958

Card 3/3

5(4)

AUTHORS: Vasil'yev, V. P., Korableva, V. D.,   SOV/153-58-3-30/30
             Yatsimirskiy, K. B.

TITLE: Conference Discussion on the Methods of Investigating the
             Complex Formation in Solutions (Soveshchaniye-diskussiya
             po metodam izucheniya kompleksoobrazovaniya v rastvorakh)

PERIODICAL: Izvestiya vysshikh uchebnykh zavedeniy. Khimiya i
             khimicheskaya tekhnologiya, 1958, Nr 3, pp 173 - 174 (USSR)

ABSTRACT: From February 18 to 21, 1958 a conference discussion took
             place at the town of Ivanovo; it dealt with the subjects
             mentioned in the title. It was called on a decision of the
             VIIth All-Union Conference on the Chemistry of Complex
             Formations. More than 200 persons attended the conference,
             among them 103 delegates from various towns of the USSR.
             At the conference methods of determining the composition of
             the complexes in solutions were discussed, as well as the
             methods of calculating the instability constants according
             to experimental data and problems concerning the influence
             of the solvent upon the processes of complex formation.
             I. I. Chernyayev, Member, Academy of Sciences, USSR, stressed
Card 1/16   in his inaugural lecture the great importance and actuality

Conference Discussion on the Methods of   SOV/153-58-3-30/30
Investigating the Complex Formation in Solutions

of the problems to be dealt with, and wished the conference
all the best in its work. I. V. Tananayev, on behalf of the
Orgkomitet (Organization Committee) held a lecture on: "The
Method of Determining the Composition of Compounds Formed in
Solutions". In his lecture, V. N. Tolmachev dealt with the
problem of the graphical interpretation of the method by
Ostromyslenskiy-Zhob. It was proved that this method can
also be used in such cases where the equilibrium of complex
formation was turned complex by the hydrolysis or dimerization
of the central ion. In the lecture by A. K. Babko and
M. M. Tananayko, "Physical and Chemical Analysis of the
Systems With 3 Colored Complexes in the Solution", the results
of a systematic investigation in copper-quinoline-salicylate,
as well as in copper-pyridine-salicylate systems by means of
the optical method were dealt with. In the lecture by Ya. A.
Fialkov the idea of a further investigation of the complex
formation processes in solutions was developed. Besides the
determination of the composition and stability of the complexes
also the physical and chemical properties, the chemical nature
Card 2/16   and the structure of the complex compounds must be investi-

Conference Discussion on the Methods of   SOV/153-58-3-30/30
Investigating the Complex Formation in Solutions

gated. The lecture by K. B. Yatsimirskiy dealt with the
conditions of checking the usefulness of the method of isomolar
series in the determination of the complex composition. To
be able to obtain objective results the position of the
maximum at various concentrations of the components must be
checked. A. K. Babko made several critical remarks concerning
the lecture by I. V. Tananayev. He pointed out that such a
method of investigation must be chosen that is connected with
the characteristic properties of the system investigated.
A. P. Komar' mentioned in his lecture that for the time being
the method by Ostromyslenskiy-Zhob is the best for determining
the complex composition, and should be employed as often as
possible. This demands, however, that all instructions con-
cerning this method are strictly obeyed. I. S. Mustafin,
L. P. Adamovich and V. I. Kuznetsov took part in the discus-
sion. K. B. Yatsimirskiy proved in his lecture "Hydrolytic
Equilibria and the Polymerization in Solutions" that, if the
hydrolysis products are polymerized, the "inclusion into the
complex" and the "formation function" at a constant pH value
are varied with the modification of the total concentration of

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Investigating the Complex Formation in Solutions

the metal. Therefore all those methods may be employed for
investigating the polymerization of this type which make the
determination of at least one of the two functions mentioned
possible. It was proved that the hypotheses on the existence
of complexes of the type "nucleus + chain members" can also
be founded from the viewpoint of structural concepts: particles
the charge of which does not exceed unity can occur as "chain
members". The usefulness of the characterization of areas of
existence of polymers by means of surface diagrams: "total
concentration of the metal - pH" was proved as well. I. I.
Alekseyeva and K. B. Yatsimirskiy in their lecture "Investiga-
tion of the Polymerization of Iso-Poly Acids in Solutions"
mentioned experimental results of the investigation of the
polymerization in solutions of molybdic acid. The authors
proved that especially the molybdic acid within a certain
range of the pH values and the concentrations exists as a
number of compounds that can be expressed by an overall formula
$MoO_4(HMoO_4)^{n-2}$. In the lecture by N. V. Aksel'rud and V. B.

Card 4/16   Spivakovskiy investigation results on basic salts taking into

Conference Discussion on the Methods of   SOV/153-58-3-30/30
Investigating the Complex Formation in Solutions

account the complex formation in solutions by means of the
potentiometric method were mentioned for systems with zinc,
cadmium and indium. In the evaluation of their results the
authors employed the method of the table difference. The
calculation of the consecutive constants was carried out
according to the interpolation formula by Newton. M. A.
Chepelevtskiy held a lecture on "pH Measurement Method of
the Solutions in Combination With the System Analysis of the
Solubility Diagram of the System Cu^{2+}-HCl - H_2O in Investiga-
ting Complex Copper Compounds in Saturated Solutions". It
was found that the substance at the bottom of the liquid is
more basic than the solution: furthermore, the increased
acidity of the solution from the viewpoint of the formation
of hydroxy-chloro complexes in the solution was explained.
V. I. Kuznetsov opened the discussion with his lecture; he
pointed out the necessity of utilizing the concepts worked
out in the investigations of the polymerization in organic
chemistry in the chemistry of polynuclear complexes. A. A.
Card 5/16   Grinberg thinks that the new approach of the hydrolysis

Conference Discussion on the Methods of   SOV/153-58-3-30/30
Investigating the Complex Formation in Solutions

investigation as developed by the Scandinavian school is of
high value. He also pointed to the necessity of studying
the kinetics of the polymerization process and a quantitative
determination of the strength of the polymers. A. K. Babko
pointed out that the study of the polymer structure was
necessary. N. P. Komar' mentioned in his lecture that the
rather widely spread polymerization type according to the
scheme "nucleus + chain members" is not obtained in all cases.
The following scientists took part in the discussion: V. N.
Tolmachev, A. V. Ablov, I. S. Mustafin, I. V. Tananayev and
K. B. Yatsimirskiy. A. K. Babko then discussed in his lecture
"Methods of Determining the Dissociation Constant of the
Complex Groups in Solutions" the main principles of determining
the instability constants. N. P. Komar' discussed in his
lecture "Calculation Methods of the Instability Constants of
the Complex Compounds According to Experimental Data" the
possibilities of using the known calculation methods of the
instability constants for various cases of the complex forma-
tion in solution. If several mononuclear complexes are formed
the displacement method by Abegg and Bodlender (completed by

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Conference Discussion on the Methods of
Investigating the Complex Formation in Solutions

A. K. Babko) cannot be recommended for the calculation of
the instability constant. The lecturer discussed the dis-
solution methods of the polynomials proposed by B'yerrum,
Leden, Rossoti, Sketchard, Edsolloy and other authors. The
constants calculated in this way are not very accurate. It
was proved that the method of successive approximations can
lead to wrong conclusions as to the chemical processes taking
place in the system investigated. The most probable value
of the physical constants can be obtained by the method of
the least squares. B. V. Ptitsyn, Ye. N. Tekster and L. I.
Vinogradova described the determination methods of the
instability constants of the oxalate complexes of niobium,
uranium and iron which are based on the investigation of the
equilibrium displacement of the complex formation by silver
ions. N. K. Bol'shakova, I. V. Tananayev and G. S. Savchenko
held a lecture on "The Role of the Time Factor in the Investiga-
tion of the Complex Formation". In the discussion on the
lectures A. A. Grinberg mentioned that due to the slow
adjustment of the equilibria the methods discussed of
determining the instability constants (palladium and cobalt

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complexes) can often not be employed. A. V. Ablov pointed
out the necessity of devising direct methods of proving the
existence of intermediate forms in a step-wise complex forma-
tion. K. B. Yatsimirskiy mentioned that the instability
constants of slowly dissociating complexes can be calculated
from thermochemical data. L. P. Adamovich, A. M. Golub
among others took part in the discussion on the lectures.
A. K. Babko requested inclusion in the next conference on the ·
chemistry of complex compounds a lecture in which various
calculation methods of the instability constants should be
discussed by the example of actual cases. This should clarify
to which divergencies of the values of the constants dif-
ferent methods of evaluating the experimental data can lead.
N. P. Komar' stressed that in the determination of the
instability constants all chemical equilibria should be taken
into account that render complex the complex formation process
in the solution, especially the hydrolysis processes of the
central ion and the addendum. In the lecture delivered by
V. M. Peshkova and A. P. Zozulya "Application of the Distribu-
Card 8/16   tion Method to the Investigation of the Stability Constants

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of Some Thorium Complex Compounds" results obtained from the
experimental investigation of the distribution of thorium
compounds in the systems: acetylacetone - benzene - water, and
2-oxy-1,4,-naphthoquinone - chloroform - water were given.
From these data the instability constants of the thorium
complexes with acetyl-acetone and 2-oxy-1,4-naphthoquinone
were calculated. I. V. Tananayev, G. S. Savchenko and Ye. V.
Goncharov held a lecture on the application of the solubility
method in the determination of the stability of complex
compounds in solutions. In this lecture also other methods
of investigating complex formation processes in the solution
were discussed (pH measurement, measurement of the optical
density, as well as of the heat of mixing). B. D. Berezin
held a lecture on the "Application of the Solubility Method
in Studying the Phthalocyanine Complexes of Metals". He
used the determined quantitative characteristics of the
reaction of the transition of the phthalocyanides of cobalt,
nickel, copper and zinc, as well as of the free phthalo-
cyanine into the sulfuric acid solution for the theoretical
reasoning, and as an experimental proof of the existence of

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π-bonds in the complexes investigated. These characteristics
also served him as a proof of new electronic formulae of
phthalocyanine and its complex derivatives. In the lecture
delivered by I. L. Krupatkin on "The Method of the Two Solvents
as a Method of Investigating the Formation and Properties of
Organic Complexes" it was proved that this method makes it
possible to determine the number of complexes formed in the
system, their composition and relative stability. V. I.
Kuznetsov, A. K. Babko, N. P. Komar', I. S. Mustafin and
Ya. I. Tur'yan took part in this discussion. In the lecture
delivered by A. A. Grinberg and S. P. Kiseleva on the complex
palladium compounds (II) with a coordination number above
four it was proved that in the case of a large chlorine and
bromine ion excess complexes with the coordination number 5
are formed. The instability constants of these complexes
were estimated. L. P. Adamovich mentioned a new manipulation
in the spectrophotometric investigation of the complex com-
pounds that can be used in systems with the formation (or
predomination) of one single complex. This method makes it
possible to determine the composition and instability constant

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of the complex. In the lecture delivered by K. B. Yatsimirskiy
and V. D. Korableva the application of the theory of crystal-
line fields for the determination of the composition and
structure of the chloride complexes of cobalt, nickel and
copper according to the absorption spectra of these complexes
was discussed. It was proved that in a hydrochloric acid
concentration above 5 mole/liter in the solution there exists
an equilibrium between the tetrahedric and octahedric form
of the cobalt chloro complexes. Yu. P. Nazarenko proved in
his lecture "The Application of Radioactive Isotopes in the
Investigation of the Solvation Equilibrium in Solutions of
Complex Compounds" the possibility of using data on the
isotope exchange to clarify the structure of the complex and
mechanism of the hydration processes. V. Klimov mentioned
in his lecture the use of radioactive isotopes in the study
of tin and antimony complexes in non-aqueous solutions. A. V.
Ablov, V. N. Tolmachev, V. I. Kuznetsov and A. M. Golub took
part in the discussion of the lectures. The usefulness of
employing the theory of the crystalline fields in explaining
the results obtained from the absorption spectra of the com-

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plex compounds was stressed. In the lecture delivered by
I. A. Shek on "The Investigation of the Complex Formation
by the Method of the Dielectric Permeability and the Polariza-
tion" the principles of the methods mentioned were presented.
This method was employed for investigating the compounds of
the type of the "affiliation" products. The lecture delivered
by I. A. Shek and Ye. Ye. Kriss "Employing the Method of the
Dielectric Constant for Investigating Complex Compounds of
the Type of Crystal Solvates in Solutions" dealt with the
investigation of the solvates of lanthanum and cerium chlorides
with ketones, as well as with the study of the compounds
formed in heterogeneous systems with tributyl phosphate and
nitric acid. V. F. Toropova gave in her lecture "The Polaro-
graphic Method of Investigating the Complex Formation in
Solutions" a survey of the applications of the polarographic
method in the study of the complex compounds, and illustrated
several fine characteristic features of this method. In the
lecture delivered by T. N. Sumarokova "The Cryoscopic Method
of Investigating the Complex Formation Reactions" a survey of
Card 12/16   the possibilities of the cryoscopic method was given, and its

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applicability in the study of several complex compounds of
stannic chloride with organic substances was proved. A. M.
Golub described the results of his investigations of thio-
cyanate complexes of several metals. A vivid discussion took
place on the lectures held. Ya. A. Fialkov and Yu. Ya.
Fialkov considered the cryoscopic method of investigating
complex compounds to be of considerable value. K. B.
Yatsimirskiy pointed out that the publication of the surveys
on individual methods of investigating the complex formation
reactions would be desired; this concerns especially the
polarographic method. The cryoscopic method should be brought
to a level that makes the calculation of the equilibrium
constants of the processes to be investigated possible. The
problem of the method of evaluating the experimental results
becomes more and more important. Many scientists use the
instability constants without taking into account the way
in which they had been obtained. The calculation methods
employed by A. M. Golub are one step back, as compared to
those employed at present. In his lecture N. P. Komar'
pointed out the extremely great importance of the mathematical

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evaluation of the results obtained, as well as of the plotting
of curves. A. K. Babko suggested selecting one or two systems
that are experimentally well investigated, and to evaluate
the results obtained according to different methods so that
it is possible to check and evaluate them. Ya. I. Tur'yan
took part in the discussion. Ya. A. Fialkov discussed in
his lecture "The Effect of the Solvent on the Complex Formation
Process as Well as on the State of Equilibrium in the Solutions
of Complex Compounds" the influence exerted by the solvents
upon the molecular state, upon the solvation of the system
components, upon the stabilization of the complexes formed
in the system, upon the step-wise dissociation of the complexes
and upon a number of other processes. The influence exercised
by the dielectric constant upon the complex formation process
was discussed. It was concluded that a direct relation does
not exist, and that the chemical nature of the solvent must
be taken into account. A. V. Ablov and L. V. Nazarova held
a lecture on "The Spectroscopic Investigation of Nickel Cobalt
'Pyridinates' in Various Solvents". The instability constants
Card 14/16   of the complexes were determined and it was proved that the

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stability of the 'pyridinates' is changed in dependence on
the solvent. Ya. I. Tur'yan in his lecture "The Influence
of the Solvent Upon the Composition and Stability of Complex
Ions" discussed the polarographic investigation method of
the chloride and thiocyanate complexes of lead in aqueous
ethanol solutions at different content of the non-aqueous
solvent and at a constant ionic strength. A step-wise
character of the complex formation was found as well as the
instability constants of the complexes. The influence of
the dielectric constant of the solution on the stability of
the investigated complexes was proved. In the lecture by
V. P. Vasil'yev on the "Investigation of Aquo Complexes in
Mixed Solvents" the main attention was devoted to the neces-
sity of the qualitative recording of the solvation effects
in the complex formation. The applicability of the polaro-
graphic method in the determination of the composition and
stability of the aquo complexes in mixed solvents was proved
and experimental material on the thermodynamics of the
dissociation of the cadmium-aquo complexes in aqueous ethanol
solutions was mentioned. V. N. Tolmachev, V. I. Kuznetsov

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       and I. V. Tananayev stressed in their lectures the necessity
       of a more complete and general investigation of the solvation
       processes. A. K. Babko and A. M. Golub pointed out the
       great importance of the investigations of the complex forma-
       tion equilibria in non-aqueous solutions, and made several
       critical comments on the lecture by Ya. I. Tur'yan. The
       following scientists took part in this discussion: L. P.
       Adamovich, O. I. Khotsyanovskiy, A. P. Moskvin and A. G.
       Mustakhov. At the final meeting of the conference A. A.
       Grinberg, Corresponding Member, AS USSR, said in his speech
       that such a conference was very urgent. A detailed discus-
       sion of the determination methods of the composition of the
       complexes, as well as of the method used in the study of the
       quantitative characteristics of the stepwise complex forma-
       tion was extremely useful for all who attended this conference.

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USCOMM-DC-60976

5(2,4)
AUTHORS: Yatsimirskiy, K. B., Korableva, V. D.   SOV/153-58-4-4/22

TITLE: Absorption Spectra of Cobalt, Nickel and Copper-Salts
              in Concentrated Hydrochloric Acid (Spektry pogloshcheniya
              rastvorov soley kobal'ta, nikelya i medi v kontsentriro-
              vannoy khloristo-vodorodnoy kislote)

PERIODICAL: Izvestiya vysshikh uchebnykh zavedeniy. Khimiya i khimiches-
              kaya tekhnologiya, 1958, Nr 4, pp 19 - 28 (USSR)

ABSTRACT: The above mentioned spectra have not yet been investigated
              as carefully as those in aqueous solutions (Refs 1-8).
              Previous investigations are continued in the present
              paper (Refs 13,14). On the basis of the spectra and
              fundamental ideas of the theory of crystalline fields
              the authors tried to ascertain the composition and
              structure of the complex compounds formed in solutions.
              The spectra were taken by means of the spectrophotometer in
              aqueous and HCl-solutions between 220 and 1200 mμ. The
              solutions used in the tests were obtained by corresponding
              dilution from initial solutions containing cobalt,

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Absorption Spectra of Cobalt, Nickel and Copper-Salts
in Concentrated Hydrochloric Acid

nickel, copper nitrate and cobalt chloride. The
spectra taken are shown in figures 1-3. A band with
an absorption maximum at 300 mμ can be seen clearly
in the spectra of the aqueous solutions of the above
nitrates. The band is characteristic of the nitrate
ion (Ref 17). It may be assumed that the formation
of the band is connected with the transition of
electrons within the ion itself, with the transition
of electrons from the nitrate ion to the metal ion, or
vice versa. The maximum at 300 mμ is shifted with in-
creasing HCl-concentration, and a new one is formed
with its center at 270 mμ for hydrochloric cobalt,
at 300 mμ for nickel, and at 380 mμ approximately for
copper. The new maximum is apparently conditioned by
the transition of electrons from the chlorine ion
to the metal ion. The formation of the new shifting
band in the ultraviolet spectral range leads to the
assumption that chlorine complexes of these metals
exist in the hydrochloric solutions of the above
mentioned three metals. Then the spectra of each of

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Absorption Spectra of Cobalt, Nickel and Copper-Salts   SOV/153-58-4-4/22
in Concentrated Hydrochloric Acid

these metals are discussed individually. The absorption
spectra obtained may be interpreted according to the
theory of the crystalline fields, if it is presupposed that
a) cobalt forms octahedral pink-colored chlorine complexes
and various tetrahedral lightblue-colored complexes from
the HCl-concentration of 5 mol/ℓ onward; b) nickel
forms various octahedral complexes $[NiCl(H_2O)_5]^+$ and
$[NiCl_2(H_2O)_4]$ in HCl-solutions; c) the copper chloride
complexes are formed step-like, being probably of
tetragonal structure. There are 9 figures, 2 tables, and
30 references, 4 of which are Soviet.

ASSOCIATION: Ivanovskiy khimiko-tekhnologicheskiy institut (Ivanovo
Institute of Chemical Technology) Kafedra analiticheskoy
khimii (Chair of Analytical Chemistry)

SUBMITTED: October 14, 1957
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5(2)

AUTHORS: Yatsimirskiy, K. B., Berezin, B. D.   SOV/153-58-4-6/22

TITLE: Indicators of the Mercurometry (Indikatory merkurimetrii)
              Communication II: Diphenyl Carbazone (Soobshcheniye II.
              Difenilkarbazon)

PERIODICAL: Izvestiya vysshikh uchebnykh zavedeniy. Khimiya i khimiches-
              kaya tekhnologiya, 1958, Nr 4, pp 35 - 42 (USSR)

ABSTRACT: Although diphenyl carbazide, according to corresponding
              publications (Ref 11), is less suitable as indicator
              for the determination of the chlorides of thallium (Ref 4),
              silver in the presence of copper (Ref 5), methyl thio-
              uracil (Ref 6), and others, diphenyl carbazone, which
              is a better mercurometric indicator, has been still
              insufficiently investigated. Blue-violet compounds are
              formed by it with Hg^{2+}, the composition of which,
              however, is unknown. Scientists also disagree as to
              the optimum pH-value in the determination of halides.
              It would be necessary to know the solubility product
              of mercury diphenyl carbazonate and the acid dissociation
Card 1/4   constant of diphenyl carbazone in order to find the

Indicators of the Mercurometry. Communication II: SOV/153-58-4-6/22
Diphenyl Carbazone

optimum concentrations of the indicator, the possible
dilutions of halide solutions and the optimum accuracy of
the methods under various conditions. Perchloric acid
and mercury perchlorate were used in the experiments.
Table 1 presents the solubility of diphenyl carbazone
in borate buffer solutions determined at 25^0. In an
alkaline medium it can be transformed into diphenyl
carbodiazone (Ref 2). K_s of diphenyl carbazone was
measured by the spectrophotometer (Table 2). The data
obtained from the two methods mentioned above were
checked (Table 3). The spectrophotometric method of
the isomolar series was applied, because the preparative
determination of the indication product of mercury ions
(II) with diphenyl carbazone is, for various reasons, very
difficult. The results are given in table 4. The
solubility product of mercury diphenyl carbazonate
was determined according to Gorbachev's method, the
latter having been modified to a certain extent. The
solubility product amounts to (Ref 17)$(6.7\pm0.7).10^{-26}$.

Card 2/6   First a calibration curve was plotted. Hg^{2+} is practically

Indicators of the Mercurometry. Communication II: SOV/153-58-4-6/22
Diphenyl Carbazone

completely bound by diphenyl carbazone at a pH of 5 approximately. The composition at pH 2 and 5 corresponds to the ratio of diphenyl carbazone:

Hg^{2+} = 2:1. The dissociation constants of diphenyl carbazone after the first step at 25° and at ionic strengths of 0,1 and near zero amounts to $(3.4\pm0.3).10^{-8}$ and $(1.1\pm0.1).10^{-8}$. There are 2 figures, 5 tables, and 18 references, 9 of which are Soviet.

ASSOCIATION: Ivanovskiy khimiko-tekhnologicheskiy institut (Ivanovo Chemo-Technological Institute) Kafedra analiticheskoy khimii (Chair of Analytic Chemistry)

SUBMITTED: September 10, 1957

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5(4)

SOV/153-58-5-2/28

AUTHORS: Yatsimirskiy, K. B., Karacheva, G. A.

TITLE: On the Change of the Entropy in Complex Forming Reactions With Complexons (Ob izmenenii entropii pri reaktsiyakh kompleksoobrazovaniya s kompleksonami)

PERIODICAL: Izvestiya vysshikh uchebnykh zavedeniy. Khimiya i khimicheskaya tekhnologiya, 1958, Nr 5, pp 13-21 (USSR)

ABSTRACT: The reactions mentioned in the title concerning mono and bivalent cations of the metals with ethylene diamine tetraacetate, are characterized by relatively low thermal effects and by considerable positive entropy changes (Refs 1,2). Thus, the entropy changes in these reactions play an important role and to a high degree determine the stability of the metal complexonates in the solutions. There are, however, no reliable data on the entropy changes in the affiliation reaction of the proton to the anions of the complexons as well as in the reactions of the complexonate formation of the trivalent metals. As for the calculation of the entropy changes besides data on the equilibria also exact data on the enthalpy change during the said process are necessary it became necessary to determine

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calorimetrically the thermal effects of the mentioned reactions
under the participation of complexons. For this purpose the
authors decided to determine by direct calorimetric measure-
ments the reaction heat in the addition of the protons to the
anions of ethylene diamine tetraacetate and of hexamethylene
diamine tetraacetate, as well as the formation heat of the
combination of aluminum with the former acetate and of calcium
with the latter. The hexamethylene diamine tetra acetic acid
was synthesized at the IREA (Institut khimicheskikh reaktivov =
Institute for Chemical Reagents) and supplied by Professor
R. P. Lastovskiy. The results obtained are given in tables
1-5, 7, 8. Data concerning the change of the heat content and
of the entropy in the dissociation of the ethylene diamine
tetraacetic acid and of hexamethylene diamine tetraacetic
acid were obtained. With the former acid the entropy in the
dissociation of the acid is changed under the separation of
the two last protons (3rd and 4th step of dissociation) by a
much higher absolute value than is the case with the first two
protons. With the last mentioned acid it may be assumed that
the entropy in the corresponding dissociation is changed in
Card 2/3   about the same degree, i. e. in the case of the separation of

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On the Change of the Entropy in Complex Forming Reactions With Complexons

one of the protons ΔS will be equal to half of the entropy
change in the separation of two protons. Furthermore the
changes of enthalpy and entropy in the formation of the
aluminum complex with the ethylene diamine tetraacetic acid
and of the calcium complex with the hexamethylene diamine
tetraacetic acid are determined. The factors were revealed
which determine the value of the entropy change in the re-
actions of the complexonate formation in aqueous solutions.
Corresponding equations were suggested. There are 2 figures,
9 tables, and 12 references, 4 of which are Soviet.

ASSOCIATION: Ivanovskiy khimiko-tekhnologicheskiy institut, Kafedra ana-
liticheskoy khimii (Ivanovo Chemo-Technological Institute,
Chair of Analytical Chemistry)

SUBMITTED: November 19, 1957

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5(2,3)

AUTHORS: Yatsimirskiy, K. B., Berezin, B. D.   SOV/153-58-6-5/22

TITLE: Indicators of Mercurimetry (Indikatory merkurimetrii).
                  III. ß-Nitroso-α-naphthol (III. ß-nitrozo-α-naftol)

ABSTRACT: Among the indicators proposed in the most recent papers
                  (Refs 1-6) and mentioned in the title, the substance mentioned
                  in the subtitle and its monobromine derivative, bromonitrosol
                  (Ref 4), have proved most useful for various applications
                  (Refs 4,7-9) in practical work. However, a number of dif-
                  ficulties still prevent their further introduction into the
                  practical field. There are no systematic quantitative investi-
                  gations into this matter, and the necessity of appropriate
                  investigations is therefore most obvious. As bromonitrosol
                  is structurally fairly similar to ß-nitroso-α-naphthol, the
                  latter was investigated. The experimental part contains dis-
                  cussions of: (1) Acid properties of ß-nitroso-α-naphthol,
                  (2) the solubility of ß-nitroso-α-mercury-naphtholate in acid
                  solutions (Tables 3,4). Table 2 presents the computed and
Card 1/3   experimentally obtained values of the dissociation constant

Indicators of Mercurimetry. III. ß-Nitroso-α-naphthol   SOV/153-58-6-5/22

of ß-nitroso-α-naphthol. Table 1 shows its solubility in
borate buffer solutions at 25°. From their results, the
authors draw the following conclusions: The qualitative
characteristics of the substances mentioned in the subtitle
and of the indication product formed by the former with
mercury-(II) ions are very close to the corresponding values
of diphenyl-carbazonium (Ref 14). Consequently, the two
indicators can be regarded as equivalent in this respect.
Diphenyl-carbazonium does, however, yield a more vividly
colored product with Hg-ions (II), and is therefore more
sensitive. The latter reaction appears instantaneously,
whereas the reaction product of ß-nitroso-naphthol tends to
form oversaturated solutions with the Hg-(II) ions. Thus
diphenyl-carbazonium is to be more highly recommended. In the
course of work, the acid dissociation constant of ß-nitroso-α-
naphthol $(2.15 \pm 0.13) \cdot 10^{-8}$ was established. From the data
on the solubility of mercury-ß-nitroso-α-naphtholate in dif-
ferent solvents, the equilibrium constant of the indication
reaction of the Hg-(II) ions with ß-nitroso-α-naphthol was
obtained (Table 4), and the solubility product $(9.7 \pm 1.2) \cdot 10^{-27}$
as well as the instability constant of mercury-ß-nitroso-α-
naphtholate $(1.2 \pm 0.2) \cdot 10^{-20}$ were determined. There are 4

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Indicators of Mercurimetry. III.β-Nitroso-α-naphthol   SOV/153-58-6-5/22

tables and 14 references, 11 of which are Soviet.

ASSOCIATION: Kafedra analiticheskoy khimii; Ivanovskiy khimiko-
tekhnologicheskiy institut (Chair of Analytical Chemistry;
Ivanovo Chemo-technological Institute)

SUBMITTED: September 10, 1957

Card 3/3

YATSIMIRSKIY K.B.

26-58-6-16/56

AUTHOR: Udal'tsova, N.I.

TITLE: Complexons in Analytical Chemistry (Kompleksony v analitiche-
             skoy khimii) International Conference in Moscow (Mezhdu-
             narodnyy simpozium v Moskve)

PERIODICAL: Priroda, 1958, Nr 6, p 74-75 (USSR)

ABSTRACT: The use of complexons in analytical chemistry and the prospective
             development of this new field was the subject of an international
             conference in November 1957 in Moscow. It was convened at the
             Institut geokhimii i analiticheskoy khimii imeni V.I. Vernad-
             skogo Akademii nauk SSSR (Moskva) (Institute of Geochemistry
             and Analytical Chemistry imeni V.I. Vernadskiy of the USSR
             Academy of Sciences)(Moscow). The Conference heard reports on:
             Theoretical questions in the chemistry of complexons; the use
             of new indicators in complexonometric titration; the application
             of complexons in the analytical chemistry of rare elements; the
             synthesis, properties and prospective use of new complexons.
             Professor K.B. Yatsimirskiy lectured on "The Thermochemistry of
             Complex Compounds with Complexons", Professor P.N. Paley on
             "Complexon III, as a Reducing Agent" and Professor R.P. Lastov-
             skiy on "Research Work in the Field of the Synthesis of New

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26-58-6-16/56

Complexons in Analytical Chemistry.   International Conference in Moscow.

Complexons and Their Investigation".   In the discussion the following prominent Soviet scientists participated: I.P. Alimarin, I.V. Tananayev, V.I. Kuznetsov, A.K. Babko, N.P.

Card 2/2   Komar' and others.

1. Chemistry-Conference   2. Chemistry-Reports

YATSIMIRSKIY, K.B.

Main variations in kinetic method of analysis. Trudy kom. anal.
khim. 8:82-87 '58.   (MIRA 11:8)
          (Chemical reaction, Rate of)

YATSIMIRSKIY, K.B.; ROSLYAKOVA, Ye.N.

Radiometric titrations using solutions of cobalt-60 complexes.
Trudy kom.anal.khim. 9:194-199 '58.   (MIRA 11:11)
(Cobalt compounds) (Radiochemistry) (Titration)

13-2-14/43

YATSIMIRSKIY, K. B.,

Yatsimirskiy, K. B. , Korableva, V. I.

AUTHORS:

TITLE: The Thiocyanate Complexes of Manganese, Iron, Cobalt and Nickel (Rodanidnyye kompleksy margantsa, zheleza, kobal'ta i nikelya)

PERIODICAL: Zhurnal Neorganicheskoy Khimii, 1958, Vol. 3, Nr 2, pp.339-345 (USSR)

ABSTRACT: The equilibrium of the complex-formation of the following systems was investigated by the colorimetric indicator-method: $M^{2+} - CNS- M^{2+} = Mn^{2+}$, Fe^{2+}, Co^{2+}, Ni^{2+}. In all tests the concentration of thiocyanate-ion amounted to 0,0004965 mol/l and the concentrations of the metal-solutions 0,02 - 1 mol/l. By the calculation of the stability constant of the complexes it is proved that only complexes of the type $M(CNS)^+$ exist. The stability constant of $FeCNS^+$ is 0,048, of $MnCNS^+$ - 0,058, of $CoCNS^+$ - 0,031 and of $NiCNS^+$ - 0,021. The comparison of these values shows that $NiCNS^+$ represents the most unstable complex. For the determination

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The Thiocyanate Complexes of Manganese, Iron, Cobalt and Nickel

of the stability of the $CuCNS^+$-complex the colorimetric indicator-method is unsuitable, as the copper-thiocyanate complex is very unstable. There are 1 figure, 1 table, and 19 references, 4 of which are Slavic.

ASSOCIATION: Ivanovo Chemical-technological Institute
               (Ivanovsky khimiko-tekhnologichesky institut)

SUBMITTED: March 25, 1957

AVAILABLE: Library of Congress

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Yatsimirskiy, K. B., Naryshkina,   78-2-15/43

AUTHORS:

TITLE: The Kinetics of the Oxidation of Thiosulfate With Hydrogen
Peroxide in the Presence of Tungstic Acid (Kinetika reaktsii
okisleniya tiosul'fata perekis'yu vodoroda v prisutstvii
vol'framovoy kisloty)

PERIODICAL: Zhurnal Neorganicheskoy Khimii, 1958, Vol. 3, Nr 2,
pp. 346-351 (USSR)

ABSTRACT: The kinetics of the oxidation of thiosulfate with hydrogen
peroxide in an acetic-acid solution in the presence of tungstic
acid was investigated. The reaction velocity was performed by
the phototurbidimetric method with a photocolorimeter ϕЭK-M
with a green filter. Between the concentration of sulfuric
acid and the optical density of the solution a linear depen-
dence was found to exist which may be expressed by the follow-
ing formula: $D = \alpha \left[SO_4^{2-} \right]$. In this formula D denotes the optic-
al density and α the proportionality factor. From this equat-
ion follows that the modification of the optical density in
the solution is proportional to the reaction velocity and can
be used for the determination of the reaction velocity of the
catalytic oxidation of thiosulfate. The authors investigated

Card 1/3

The Kinetics of the Oxidation of Thiosulfate With Hydrogen   78-2-15/43
Peroxide in the Presence of Tungstic Acid

the dependence of the reaction velocity on the sodium-
-tungstate concentration in a quantity of $1,0.10^{-7} - 5,0.10^{-7}$
mol/l and on the concentration of H_2O_2 in a quantity of
$0,8.10^{-3} - 7,2.10^{-3}$ mol/l as well as on the concentration of
sodium thiosulfate in a quantity of $0,8.10^{-3} - 3,6.10^{-3}$ mol/l.
The reaction velocity of the concentration of hydrogen ions
was also investigated as well as the influence exerted by
various additions. The reaction velocity of the catalytic oxi-
dation of thiosulfate with H_2O_2 may generally be expressed
by the following equation:

$$\frac{d\left[SO_4{}^{2-}\right]}{dt} = \kappa \cdot c_W{}^q \cdot c_{S_2O_3}{}^{2-} \cdot c_{H_2O_2}^p .$$ In this equation denotes κ

the catalytic coefficient and q, m and p are the power expon-
ents. The performed tests show that the reaction velocity
shows a linear dependence on the sodium-tungstate concentrat-
ion and the hydrogen-peroxide concentration. But the depen-
dence on sodium thiosulfate is of a complicated nature. The
reaction velocity of the catalytic oxidation of sodium thio-
sulfate with hydrogen peroxide increases with an increase in
the concentration of hydrogen ions. In an acid medium tungstic

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78-2-15/43

The Kinetics of the Oxidation of Thiosulfate With Hydrogen
Peroxide in the Presence of Tungstic Acid

Acid is converted to various cationidic forms, e.g.:

$H_2WO_4 + H^+ = WO_2 \cdot OH^+ + H_2O$, $H_2WO_4 + 2H^+ = WO_2^{2+} + 2 H_2O$.

The catalytic oxidation of sodium thiosulfate with H_2O_2 in
an acid medium probably is a reaction between ions with oppo-
site poles. At first the cationidic forms of tungstic acid re-
act with hydrogen peroxide under complex-formation and then the
slow reaction between this complex $[WO_2OHH_2O_2^+]$ and hydrothio-
sulfate $[HS_2O_3^-]$. There are 10 figures, 1 table and 10 re-
ferences, 5 of which are Slavic.

ASSOCIATION: Ivanovo Chemical-technological Institute   (Ivanovskiy
khimiko-tekhnologicheski institut)

SUBMITTED: April 24, 1957

AVAILABLE: Library of Congress

Card 3/3

78-2-16/43

YATSIMIRSKIY, K.B.

AUTHORS: Yatsimirskiy, K. B. , Karacheva, G. A.

TITLE: The Kinetics of the Oxidation Reaction of Iodide With Hydrogen Peroxide in the Presence of Iron-/III/-Compounds (Kinetika reaktsii okisleniya yodida perekis'yu vodoroda v prisutstvii soyedineniy zheleza (III))

ABSTRACT: The authors determined the kinetics between hydrogen peroxide and potassium iodide in the presence of iron salts in HCl- and H_2SO_4-solutions. The investigation of the kinetics of this reaction was performed by the optical method. The photometric investigations were performed on a universal photometer of the type φM with green filter and at 533 μμ and 19-20°C and 21-22°C. The inclination between the tangent angle and the abscissa of the iron-concentration is proportional to the reaction velocity.

$$tg\,\alpha \; = \; \frac{dD}{dt} \; = \; \varepsilon \cdot \mathcal{l} \cdot \frac{dc}{dt} \; = \; \varepsilon \cdot \mathcal{l} \cdot v$$

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The Kinetics of the Oxidation Reaction of Iodide With Hydrogen Peroxide in the Presence of Iron-/III/-Compounds

d = optical density, t = time, $\mathcal{E}$ = molar coefficient, ℓ = thickness of layer, v = reaction velocity, The dependence of the reaction velocity on the iron-concentration, the concentration of hydrogen ions, the concentration of potassium iodide and the HCl-concentration was illustrated by experiments. Analogous tests were also performed with sulfuric acid and iron-/III/-sulfate as catalysts. The kinetic equation of the catalytic reaction is as follows:

$$\frac{dc_{J_2}}{dt} = \mathcal{X} c_{H_2O_2}^m \cdot c_{J^-}^n \cdot c_{Fe^{3+}}^k$$

In this formula $\mathcal{X}$ = the catalytic coefficient, C_{J_2}, $C_{H_2O_2}$, C_{J^-} and $C_{Fe^{3+}}$ signify concentrations of the corresponding ions in the reaction mixture. The reaction intermixture increases with an increase in the concentration of hydrochloric acid. The reaction velocity in the case of H_2SO_4 is complicated, as sulfuric-acid complexes form on these conditions. The stability of trivalent iron with ethylene-diamine-tetraacetic acid was also determined by the kinetic method. For pK, Fe, EDTA at μ = 0 a value of 26,5 - 27,8 was found. There are 9 fi-

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78-2-16/43

The Kinetics of the Oxidation Reaction of Iodide With Hydrogen Peroxide in the Presence of Iron-/III/-Compounds

gures, 3 tables, and 12 references, 2 of which are Slavic.

ASSOCIATION: Ivanovo Chemical-technological Institute
(Ivanovskiy khimiko-tekhnologicheskiy institut)

SUBMITTED: April 24, 1957

AVAILABLE: Library of Congress

Card 3/3

SOV/78-3-8-46/48

AUTHORS: Vasil'yev, V. P., Korableva, V. D., Yatsimirskiy, K. B.

TITLE: Conference Discussion on the Methods of Investigating Complex
              Formations in Solutions (Soveshchaniye-diskussiya po metodam
              izucheniya kompleksoobrazovaniya v rastvorakh)

PERIODICAL: Zhurnal neorganicheskoy khimii, 1958, Vol. 3, Nr 8, pp. 1982-
              1986 (USSR)

ABSTRACT: From February 18 - 21, 1958 a conference with discussions took
              place at Ivanovo, which dealt with the methods of investigating
              the complex formations in solutions.
              At this conference the methods of determining the composition
              of the complexes in solutions, the methods of calculating the
              stability constants on the basis of experimental data, as well
              as the influence exerted by the solvents on the process of com-
              plex formation were discussed. Numerous experimental and theo-
              retical papers were submitted to the conference, which dealt
              with the process of complex formation in aqueous and non-aqueous
              solutions. Especially methods concerning the composition of the
              complexes as well as methods of investigating step-wise complex
              formations were dealt with in detail.

Card 1/2

SOV/78-3-10-5/35

AUTHOR: Yatsimirskiy, K. B.

TITLE: The Thermochemistry of the Compounds of Transition Metals and
              the Theory of the Crystal Fields (Termokhimiya soyedineniy
              perekhodnykh metallov i teoriya kristallicheskikh poley)

PERIODICAL: Zhurnal neorganicheskoy khimii, 1958, Vol 3, Nr 10, pp 2244-2252
              (USSR)

ABSTRACT: The thermochemistry and the theory of the crystal field were used
              for the thermochemical characterization of the solid compounds
              of transition metals. An analysis was carried out of the struc-
              ture and energetic curve of some ions of transition metals, as
              well as of the lattice energy of the chlorides of elements of
              the fourth and fifth group of the periodic system. The effective
              energy of this compound is $\Delta = \varrho(E_2 - E_1)$ (6). The difference
              between the value of lattice energy determined by experiments
              and that calculated by linear interpolation is represented by the
              magnitude Δ. The magnitude Δ shows constant values for most of
              the salts of iron-(II), cobalt-(II), nickel and copper. The
              values of Δ calculated by the thermochemical analysis are
              higher than those obtained by the optical analysis. The magnitude
              Δ shows higher values for trivalent elements than for bivalent

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SOV/78-3-10-5/35

The Thermochemistry of the Compounds of Transition Metals and the Theory of the Crystal Fields

ones. Δ is higher for the compounds of elements of the fifth period than for those belonging to the fourth period. The values of lattice energy for many compounds of the fourth group of the periodic system are indicated in the tables 3 and 4. The increase of lattice energy of fluorides, sulfides and sulfates of the fourth group of the periodic system was calculated and indicated in table 6. It was shown that chlorides, bromides, iodides, oxides, hydroxides and acid salts of elements of the fourth group of the periodic system (Mn, Fe, Co, Ni, Cu, Zn) show a constant difference of heat of formation for one metal and one pair of anions. This rule was used for the calculation of the unknown heat of formation of $Fe(HCO_2)_2$, $Fe(NO_3)_2$ and $NiCO_3$. There are 2 figures, 9 tables, and 18 references, 5 of which are Soviet.

ASSOCIATION: Ivanovskiy khimiko-tekhnologicheskiy institut (Ivanovo Institute of Chemical Technology)

SUBMITTED: August 6, 1957

Card 2/2

YATSIMIRSKIY, K.B.

75-1-18/26

AUTHORS: Yatsimirskiy, K. B., Rigin, V. I.

TITLE: Kinetic Methods of Quantitative Analysis
             (Kineticheskiye metody kolichestvennogo analiza).
             Report   4. Determination of Small Amounts of
             Tungsten (Soobscheniye 4. Opredeleniye malykh
             kolichestv vol'frama)

PERIODICAL: Zhurnal Analiticheskoy Khimii, 1958, Vol. 13, Nr 1,
             pp. 112-115 (USSR)

ABSTRACT: A number of elements can be quantitatively determined by
             utilizing their catalytic action upon reactions whose
             velocities are comparativele low and conveniently measurable.
             The oxidation of iodides with hydrogen peroxide in acid
             solutions:

$$H_2O_2 + 2J^- + 2H^+ = J_2 + 2H_2O \quad (1)$$
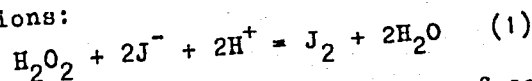
             at room temperature in the absence of catalysts proceeds
             very slowly. It was found that the reaction velocity
             in the presence of traces of hexavalent molybdenum and
             tungsten compounds, but also of compounds of iron, uranium

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Kinetic Methods of Quantitative Analysis.
Communication 4. Determination of Small Amounts of Tungsten

and chromium is higher. The catalysis of the reaction by molybdates can be used for the determination of molybdenum (ref. 5). In the present paper a method for the quantitative determination of small amounts of tungsten is described. On the basis of experimental results the following equation was set up for the velocity of the catalyzed reaction (1):

$$\frac{d\ J_2}{d\ \tau} = \varkappa \cdot c_{J^-} \cdot c_{H_2O_2} \cdot c_W \quad (2)$$

$\varkappa$ is the coefficient of the catalysis and is dependent on acidity. This may be explained by the fact that only forms with tungsten as cation are catalytically active and that an increase in the acid concentration increase the concentration of these forms and possibly also modifies their structure. For 0,1 molar acid concentration $\varkappa$ according to equation (2) is equal to $1,0.10^8$ (time in minutes, contentration in moles per liter).
On the basis of theoretical considerations

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Kinetic Methods of Quantitative Analysis.
Report   4. Determination of Small Amounts of Tungsten

the minimum tungsten concentration can be determined
which can be found by this method. For this the velocity
constant k of the non-catalyzed reaction is needed. Under
the same conditions it is according to published data
(ref. 2) equal to 1,89. Consequently the following applies
for the minimum concentration of tungsten ($c_{W_{min}}$):

$$c_{W_{min}} \geqslant 0,1 \frac{k}{\chi} \approx 2.10^{-9} \text{ mol/liter}$$

There-fore, regarding sensitivity, this method surpasses
all hitherto known methods of determining tungsten. By
this method tungsten can also be determined in the presense
of a number of other elements. Calcium, aluminum, zinc,
nickel, cobalt and manganese at the concentrations
investigated (ratio $c_{foreign \ ion} : c_{tungsten} = 10^6$) exercise
no essential influence on t reaction velocity. On the basis

Card 3/5   of the reaction $2Cu^{2+} + 4J^- \longrightarrow Cu_2J_2 + J_2$ copper slightly

75-1-18/26

Kinetic Methods of Quantitative Analysis.
Report   4. Determination of Small Amounts of Tungsten

accelerates the separation of iodine. Lead, mercury and cadmium slow down the reaction, because they form complex ions with the iodide and thereby diminish the effective concentration of the iodide. Phosphate retards the reaction. Fluoride, citrate, tartrate, oxalate, arsenate and silicate at the investigated concentrations (ratio $c_{foreign}$: $c_{tungsten}$ = 10^3) completely prevent the catalytic action of tungsten. The solubility of tungstic acid H_2WO_4 and mercury (I) - tungstate was also determined according to this kinetic method. Only scarce and contradictory data exist on the solubility of these compounds which form the precipitate in the gravimetric determination of tungsten. For the solubility of tungstic acid in 1-normal hydrochloric acid the authors found $(1,0 \pm 0,1) \cdot 10^{-4}$ mole/liter and for the solubility of mercury (I)-tungstate in 1-normal hydrochloric acid they found $(2,2 \pm 0,2) \cdot 10^{-4}$. In an experimental part the investigations of the dependence of the reaction velocity of the catalyzed reaction(1) on the concentrations of tungsten, iodide, hydrogen peroxide as well as hydro-

Card 4/5

Kinetic Methods of Quantitative Analysis.   75-1-18/26
Report   4. Determination of Small Amounts of Tungsten

chloric acid are described in detail. The experiments on
the influence of foreign ions upon the determination and
the experiments for the determination of the solubility
of tungstic acid and its mercury (I)-salt are also
described.
There are 5 figures, 4 tables, and 8 references, 3 of which
are Slavic.

ASSOCIATION: Ivanovo Chemical and Technological Institute
               (Ivanovskiy khimiko-tekhnologicheskiy institut)

SUBMITTED: March 2, 1957

AVAILABLE: Library of Congress

              1.   Tungsten - Determination   2.   Quantitative
                   analysis - Methods

Card 5/5

YATSIMIRSKIY, K.B.

P.2

75-13-2-24/27

AUTHOR: Pozdnyakov, A.A.

TITLE: Symposium on the Theory and Use of Complexons in
               Analytical Chemistry (Simpozium po teorii i primeneniyu
               kompleksonov v analiticheskoy khimii)

PERIODICAL: Zhurnal Analiticheskoy Khimii, 1958, Vol. 13, Nr 2,
               pp. 261-262 (USSR)

ABSTRACT: A symposium on the theory and the use of complexons
               in analytical chemistry which was called by the Commission
               for Analytical Chemistry at the Institute for Geoche-
               mistry and Analytical Chemistry imeni V.I. Vernadskiy
               AS USSR, took place in Moscow from November 28 to
               November 30, 1957. More than 50 specialists of complexo-
               metry, amongst whom were also representatives from people's
               democracies, attended this symposium. 13 lectures were
               attended and judged. Part of the reports was devoted to
               theoretical problems, another part dealt with the synthesis

Card 1/4

75-13-2-24/27

Symposium on the Theory and Use of Complexons in Analytical Chemistry

of new complexons and color indicators and with the use of complexons, especially of complexon III, for the separation and determination of elements.
K.B. Yatsimirskiy (Ivanovo) reported on the results of thermochemical investigations of complex compounds.
R. Prshibil (Prague) reported on metallochromic indicators of the phthalein-series and on 2 new indicators: Glycine-thymol-blue and glycine-cresol-red. I.Kerbl (Prague) reported on the results obtained by the investigation of metallochromic derivatives of amino acids and on the mechanismn of the indicator effect of metallochromic indicators. One of the articles by this author dealt with errors in titration in complexometry. The reports delivered by L. Erdei (Budapest) and I.M. Mustafin (Saratov) were devoted to the use of some new indicators

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75-13-2-24/27

Symposium on the Theory and Use of Complexons in Analytical Chemistry

in complexometry. R. Prshibil reported on the complexo-
metric determination of oxydizing and reducing compounds.
P.N. Paley (Moscow) reported about the reducing properties
of complexon III. R.P. Lastovskiy (Moscow) reported on
investigation works in the field of the synthesis of new
complexons and their investigation. Lyan' Shi-tsyuan' and
Tsen' In'-tsao (Peking) reported on the possibility of
the use of the complexes of pyrocatechol with trivalent
iron for the determination of fluorine.M.M. Senyavin
(Moscow) delivered a lecture on the use of complexons
in the ion exchange chromatography. Yu.Yu. Lur'ye
(Moscow) reported on some methods of analysis in the
metallurgy of nonferrous metals which are based on the
use of complexon III. In the course of a discussion,
A.K. Babko proposed to use complexon III for the retardation
of crystallization processes.

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75-13-2-24/27

Symposium on the Theory and Use of Complexons in Analytical Chemistry

I.P. Alimarin, I.V. Tananayev, V.I. Kuznetsov, A.K. Babko, N.P. Komar' and others took an active part in the symposium.

1. Chemistry--USSR

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5(2)
AUTHORS: Yatsimirskiy, K.B., Alekseyeva, I.I.   SOV/32-24-12-2/45

TITLE: Spectrophotometric and Kinetic Methods for Determining Molybdenum
            in Alloys (Spektrofotometricheskiy i kineticheskiy metody opre-
            deleniya molibdena v splavakh)

PERIODICAL: Zavodskaya Laboratoriya, 1958, Vol 24, Nr 12, pp 1427-1429 (USSR)

ABSTRACT: A method for determining molybdenum in steels and nickel alloys was
            developed which is based upon the absorption of light by molybdic
            acid in the wave-length region 220 - 240 mμ (Ref 2). It is carried
            out in alkaline medium. The sensitivity of the method is given as
            $7 \cdot 10^{-7}$ g/ml Mo. The measurements were made with a SF-4 spectrophoto-
            meter. The molybdenum content is determined on the basis of a standard
            curve. Molybdenum alloys of Ni base Nr 3 and 4 as well as EI401 and
            Kh10S2M steels were analyzed (Table 1). The relative error of the meth-
            is 2-5 %. The kinetic method of determining molybdenum is ten times
            more sensitive than the spectrophotometric method. The principle of
            the kinetic method is the catalytic effect of molybdic acid in the
            oxidation of iodide with hydrogen peroxide. The method was pre-
            viously reported in an earlier paper (Ref 5).

Card 1/2   Since Fe^{3+}, Cu^{2+}, and other ions interfere in the analysis the iron

Spectrophotometric and Kinetic Methods for Determining Molybdenum in Alloys

SOV/32-24-12-2/45

(Fe^{2+}) in the present analysis was oxidized with Trilon B to Fe^{3+} and then bound in a complex compound. A FEK-M apparatus was used to analyze Kh 10S 2 M steel (Table 2) and iron oxide (Fe_2O_3) (Table 3).

The sensitivity of the method is about 10^{-8} g/ml Mo.- There are 3 tables and 7 references, 6 of which are Soviet.

ASSOCIATION: Ivanovskiy khimiko-tekhnologicheskiy institut
(Ivanovo Chemical Technological Institute)

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PHASE I BOOK EXPLOITATION   SOV/2032

5(3)

Yatsimirskiy, Konstantin Borisovich, and Vladimir Pavlovich Vasil'yev

Konstanty nestoykosti kompleksnykh soyedineniy (Instability Constants of Complex Compounds) Moscow, Izd-vo AN SSSR, 1959. 205 p. 4,500 copies printed. Errata slip inserted.

Sponsoring Agency: Akademiya nauk SSSR. Institut obshchey i neorganicheskoy khimii.

Resp. Ed.: I.I. Chernyayev, Academician; Ed. of Publishing House: D.N. Trifonov; Tech. Ed.: S.G. Markovich.

PURPOSE: The book is intended for chemists, engineers, and technicians concerned with analytical chemistry, electro-chemistry, technology of nonferrous and rare metals, and related fields.

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Instability Constants (Cont.)   SOV/2032

COVERAGE: The authors claim that this book is the first
    attempt to make a complete compilation of the instability
    constants of complex compounds. Instability constants of
    1,381 complex compounds are given. Methods of calculating
    instability constants are described in an introductory
    chapter. The book was compiled chiefly on the basis of
    literature published up to 1954. No personalities are
    mentioned. There are 79 references, of which 35 are
    Soviet, 28 English, 6 German, 4 French, and 6 Swedish.

TABLE OF CONTENTS:

Card 2/10

Yatsimirskiy, K. B.

5(4)   SOV/153-2-4-2/32

AUTHOR: Yatsimirskiy, K. B.

TITLE: Thermochemistry of the Dissociation of Hydrogen Peroxide

PERIODICAL: Izvestiya vysshikh uchebnykh zavedeniy. Khimiya i khimicheskaya
               tekhnologiya, 1959, Vol 2, Nr 4, pp 480 - 484 (USSR)

ABSTRACT: The author computes the formation heats of the ions and radicals
               formed with the dissociation mentioned in the title, according
               to various schemes. Depending on the bursting point of the che-
               mical bond, the following groups may form with the dissociation
               of the H_2O_2 molecule. H^+, O_2H^-, H,H^-, O_2H, O_2H^+, OH^-, HO^+ and OH
               (Ref 1). If the dissociation of the latter continues, new atoms
               and ions may appear: O, O^-, O_2^- and O_2^{2-}. In order to compute
               the heat effects of the dissociation reactions of H_2O_2 in the
               gaseous phase and an aqueous solution, the formation heats of
               the particles mentioned above have to be known. The data on
               aqueous H_2O_2-solutions are rather scarce. However, these values
               can be estimated on account of the present laws and rules together
Card 1/3   with thermochemical data. Table 1 shows the formation heats of

Thermochemistry of the Dissociation of Hydrogen Peroxide SOV/153-2-4-2/32

O^+, OH^+, O_2H_2 and O^{2-}, in addition to most particles mentioned above. The formation heats of the gaseous ions O_2^- and O_2^{2-} can be determined (Table 2) from the formation heats of the corresponding crystalline compounds of alkali metals (Ref 3) as well as from the values of the lattice energy (Refs 7 and 10). The values of proton affinity computed by the author are shown in table 1. It is necessary to know the hydration heats of the respective particles in order to compute the heat effects of the dissociation reactions of H_2O_2 in aqueous solution. The hydration heats of only four of the groups mentioned are given in publications. In order to estimate the hydration heat, the dimensions of the respective particles have to be determined and, occasionally, their shape has to be considered. Since the size of the anions O^{2-} and OH^- is approximately equal, the author assumed that the particle size OH^m and O_2H^m depends only slightly on their charge. Thus the effective cationic radii of OH^+ and O_2H^+ were equated to 1.3 and 1.7 Å, respectively; their hydration heats, however, to those of $-K^+$ and Cs^+. A round value of 10 kcal/mol was assumed for OH and O_2H, and of 4 kcal/mol for the hydration heats of U and O. The hydration heat of H^- was determined by interpolation

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Thermochemistry of the Dissociation of Hydrogen Peroxide SOV/153-2-4-2/32

by using the values of the ionic radii of F^-, H^- and Cl^- as well as of the hydration heats of F^- and Cl^-. The average value of the heats of F^- and OH^- was assumed to be the value of the hydration heat of O^-. The hydration heats of the ions O_2^- and O_2^{2-} was also determined by interpolation. The formation heat of particles in an aqueous solution could be computed according to equation (3) since there were data available on the formation and hydration heats. The last column of table 1 shows these values for all particles mentioned. These values can be used for computing the heat effects of the dissociation of H_2O_2 and of several ions and radicals. Table 3 shows a summary arranged according to various schemes in the gaseous phase and in aqueous solution. All H_2O_2 reactions are endothermal according to these schemes. There are 3 tables and 12 references, 5 of which are Soviet.

ASSOCIATION: Ivanovskiy khimiko-tekhnologicheskiy institut, Kafedra analiticheskoy khimii (Ivanovo Institute of Chemical Technology, Chair of Analytical Chemistry)

SUBMITTED: December 27, 1957

Card 3/3

5(4)

SOV/63-4-2-8/39

AUTHOR: Yatsimirskiy, K.B., Professor

TITLE: Kinetic Methods of Chemical Analysis

ABSTRACT: The rate of chemical reactions can be used to determine the concentration
             of the reacting substances. This kinetic method is very sensitive and
             selective. Quantities of 10^{-11}-10^{-12} g and concentrations of 10^{-8}-10^{-9} M
             can be determined. Drawbacks are the high relative error of 5 - 7%, the
             effect of temperature admixtures, the surface of the reaction vessel, etc.
             A formula is given for determining the concentration of a substance B
             by obtaining the rate of change of the substance A. The reactions used
             in the kinetic method are usually of the homogeneous catalytic oxidation-
             reduction type. Some substances are determined by their ability to form
             inactive compounds which stop the catalytic reaction $\underline{/}$Ref 9, 15$\underline{/}$.
             The reaction rate is measured according to the law Lambert-Buger-Baer.
             Reactions in which light-absorbing substance forms or disappears are
             especially useful, because the optical density changes during the re-
             action. Reactions in which gases are formed $\underline{/}$Ref 21$\underline{/}$ are used in the

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Kinetic Methods of Chemical Analysis   SOV/63-4-2-8/39

kinetic method by obtaining the volume of the gas at certain time in-
tervals. If the concentrations of the tested substances vary only
slightly, the differential method of kinetic analysis must be applied.
If the variation is considerable, the integral method is used. For-
mulae are given. In a table the various methods for determining dif-
ferent elements and ions are compiled. The absence of catalytic ac-
tivity in various complex metal compounds, the simple compounds of which
are catalytically active, is used in the study of complex formation
$\sqrt{\text{Ref}}$ 32, 43, 63, 69, 70$\sqrt{}$.
There is 1 table and 72 references, 24 are Soviet, 21 Japanese, 10
German, 6 American, 4 English, 3 Italian, 1 Hungarian, 1 Yugoslav,
1 Polish, and 1 Czechoslovak   .

Card 2/2

SOV/78-4-2-9/40

· 5(4)·
AUTHORS: Yatsimirskiy, K. B., Karacheva, G. A.

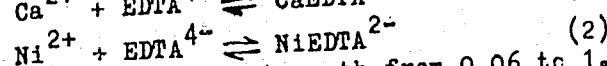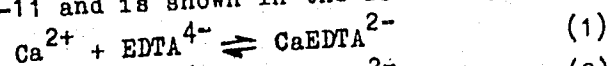TITLE: On the Influence of   Ionic Strength on the Heat
              Effect in the Formation Reaction of the Complexonates of
              Calcium and Nickel (O vliyanii ionnoy sily na teplovoy effekt
              reaktsii obrazovaniya kompleksonatov kal'tsiya i nikelya)

PERIODICAL: Zhurnal neorganicheskoy khimii, 1959, Vol 4, Nr 2,
              pp 294-300 (USSR)

ABSTRACT: The influence of the ionic strength   on the change of the
              entropy and heat content during the complex forming reactions
              of calcium and nickel was investigated by ethylenediamine
              tetraacetic acid. The complex formation proceeds quantitatively
              at pH 10-11 and is shown in the following equations:
$$Ca^{2+} + EDTA^{4-} \rightleftarrows CaEDTA^{2-} \qquad (1)$$
$$Ni^{2+} + EDTA^{4-} \rightleftarrows NiEDTA^{2-} \qquad (2)$$
              The change of the ionic strength from 0.06 to 1.58 brings
              about a considerable change of ΔH and ΔZ whereas the entropy
              change ΔS almost remains constant. It was found that at low
              ionic strengths (up to 0.15) the entropy change decreases with

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On the Influence of   Ionic Strength   on th Heat   Effect in the
Formation Reaction or the Complexonates of Calcium and Nickel

an increase in ionic power. The average entropy change on the
formation of the complex CaEDTA^{2-} is 30.6 $\pm$ 0.2 cal/mol degrees.

For ΔH of the formation of CaEDTA^{2-} the following equation
was found:
$$\Delta H = f(\mu) - 8.16 \qquad (10) \quad \mu.... \text{ ionic strength}$$
On the change of the thermodynamic functions analogous
regularities of the formation of the complex NiEDTA^{2-} were
found. Here, the average entropy change is 59.2 $\pm$ 0.5 cal/mol
degrees.

The following equation was found for ΔH:
$$\Delta H = f(\mu) - 10.08 \qquad (11)$$
The ΔH values found experimentally and the ΔH values cal-
culated from equations (10) and (11), of respective ionic
strengths, are in accordance. The difference between experi-
mental values and values calculated does not exceed

$\pm$ 0.1 kcal/mol in the case of complex CaEDTA^{2-} and

Card 2/3 $\pm$ 0.2 kcal/mol in the case of NiEDTA^{2-}. There are 3 figures,

SOV/78-4-2-9/40

On the Influence of Ionic Strength on th Heat Effect in the Formation Reaction of the Complexonates of Calcium and Nickel

6 tables, and 11 references, 2 of which are Soviet.

ASSOCIATION: Ivanovskiy khimiko-tekhnologicheskiy institut (Ivanovo Chemo-technological Institute)

SUBMITTED: August 6, 1957

Card 3/3

5(4)
AUTHORS: Yatsimirskiy, K. B., Orlova, M. N.   SOV/78-4-4-6/44

TITLE: The Influence of Gold Compounds on the Velocity of the
             Substitution   Reaction in Cyanide Complexes of Iron (II)
             (Vliyaniye soyedineniy zolota na skorost' reaktsii
             zameshcheniya v tsianidnykh kompleksakh zheleza (II))

PERIODICAL: Zhurnal neorganicheskoy khimii, 1959, Vol 4, Nr 4,
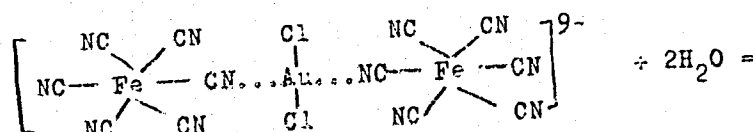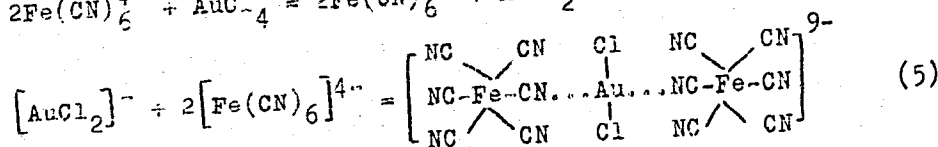   pp 741-746 (USSR)
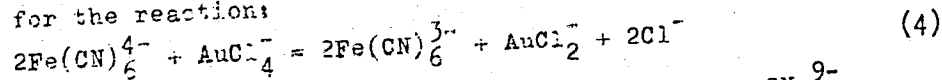
ABSTRACT: The kinetics of the reaction between ferrocyanide and
             nitroso benzene in the presence of gold compounds was
             investigated by using optical methods. The light
             absorption of the complex compound formed between iron
             aquopentacyanide and nitroso benzene was investigated.
             The absorption spectrum was plotted at a wave length of
             530 mμ using a FEK-N-54 nephelometer. It was found that
             the reaction between the ferrocyanide ions and the
             nitroso benzene in the presence of gold salts is not
             a catalytic reaction. The reaction proceeds at first
             through an oxidation of the ferrocyanide and a
             simultaneous reduction of the gold (III) to gold (I).
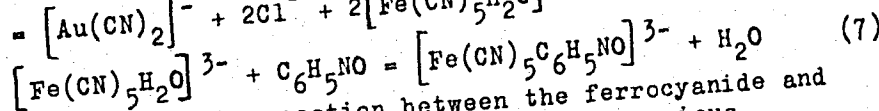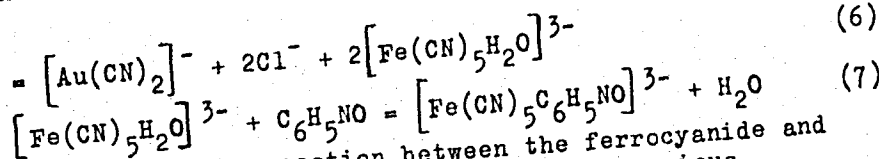
Card 1/4

The Influence of Gold Compounds on the Velocity of   SOV/78-4-4-6/44
the Substitution Reaction in Cyanide Complexes of Iron (II)

In the second stage of the reaction the ferrocyanide
and gold chloride form an intermediate complex, which
in aqueous solution decomposes into the ions $[Fe(CN)_5 H_2O]^{3-}$
and $[Au(CN)_2]^-$. The ferroaquopentacyanide ion reacts
rapidly with nitroso benzene to form the colored complex
$[Fe(CN)_5C_6H_5NO]^{3-}$. The following mechanism is suggested
for the reaction:

$$2Fe(CN)_6^{4-} + AuCl_4^- = 2Fe(CN)_6^{3-} + AuCl_2^- + 2Cl^- \qquad (4)$$

$$[AuCl_2]^- + 2[Fe(CN)_6]^{4-} = \left[\begin{matrix} NC & CN & Cl & NC & CN \\ NC-Fe-CN...Au...NC-Fe-CN \\ NC & CN & Cl & NC & CN \end{matrix} \right]^{9-} \qquad (5)$$

$$\left[\begin{matrix} NC & CN & Cl & NC & CN \\ NC-Fe-CN...Au...NC-Fe-CN \\ NC & CN & Cl & NC & CN \end{matrix} \right]^{9-} + 2H_2O =$$

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The Influence of Gold Compounds on the Velocity of   SOV/78-4-4-6/44
the Substitution Reaction in Cyanide Complexes of Iron (II)

$$= \left[Au(CN)_2\right]^- + 2Cl^- + 2\left[Fe(CN)_5H_2O\right]^{3-} \qquad (6)$$

$$\left[Fe(CN)_5H_2O\right]^{3-} + C_6H_5NO = \left[Fe(CN)_5C_6H_5NO\right]^{3-} + H_2O \qquad (7)$$

The rate of the reaction between the ferrocyanide and
the nitroso benzene was investigated at various
concentrations of gold salts and ferrocyanide ions
and at various pH values. The results are given in figure
1. The maximum rate of reaction occurs in the p_H range
4.2 to 5. In more strongly acidic and basic solution
the rate of reaction is slower. The intensity of the
violet color of the complex $\left[Fe(CN)_5C_6H_5NO\right]^{3-}$ is
dependent upon the gold concentration. The influence of
various salts upon the reaction was investigated. The
salts KNO_3, KCl, and KBr do not influence the formation
of the complex. The presence of KCN and KCNS disturbs
the reaction, since in this case the gold ion is bound

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The Influence of Gold Compounds on the Velocity   SOV/78-4-4-6/44
the Substitution Reaction in Cyanide Complexes of Iron (II)

in very stable complexes. The rate constants of the
reaction were determined for various pH values. Mercury
and platinum ions disturb this determination of gold.
There are 7 figures and 9 references.

ASSOCIATION: Ivanovskiy khimiko-tekhnologicheskiy institut
(Ivanovo Chemical Technological Institute)

SUBMITTED: January 13, 1958

Card 4/4

SOV/78-4-4-18/44

5(4)
AUTHORS:

Yatsimirskiy, K. B.; Alekseyeva, I. I.

TITLE:

State   f Molybdic Acid in Weak   Acid Solutions
(U sostoyanii molibdencvoy kisloty v slabokislykh rastvorakh)
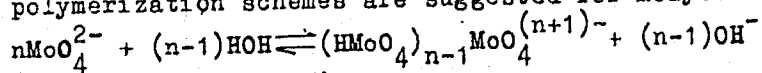
PERIODICAL:

ABSTRACT:

The conditions under which molybdic acid polymerizes were in-
vestigated at different concentrations ($2.0 \cdot 10^{-4}$ to $8.0 \cdot 10^{-2}$
molar) and at various pH values (1-6.5). In order to ascertain
the possibility of the existence of the monomeric form of
molybdic acid and to determine the nature of the polymerization
process the light absorption of solutions of molybdates and
molybdic acid was studied at wavelengths from 270 to 350 mμ.
The determination of the optical densities was carried out
using a SF-4 spectrophotometer. The dependence of the molar
absorption coefficients upon the molybdate concentration was
investigated at constant pH and constant wavelength. The curves
obtained show that at lower molybdate concentrations the
molybdic acid is present in the monomeric form. The polymeric
form exists also at higher concentrations. The phase diagram
of molybdic acid in solution was constructed (log C in
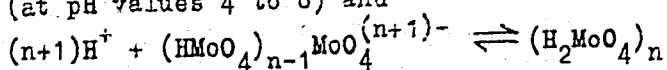
Card 1/2

SOV/78-4-4-18/44

State   Molybdic Acid in Weakly Acid Solution

dependence upon the pH value). In the pH range 1 to 4 the polymerization begins at a molybdic acid concentration of 10^{-3} molar. With an increase in the pH value the polymerization boundary shifts to the side of the higher concentration. Finally at pH 6.5 no more polymerization occurs. The following polymerization schemes are suggested for molybdic acid:

$$n MoO_4^{2-} + (n-1)HOH \rightleftharpoons (HMoO_4)_{n-1} MoO_4^{(n+1)-} + (n-1)OH^-$$

(at pH values 4 to 6) and

$$(n+1)H^+ + (HMoO_4)_{n-1} MoO_4^{(n+1)-} \rightleftharpoons (H_2MoO_4)_n$$

(at pH values 1-4).
There are 5 figures and 7 references, 1 of which is Soviet.

ASSOCIATION: Ivanovskiy khimiko-tekhnologicheskiy institut (Ivanovo Chemical Technological Institute)

SUBMITTED: April 24, 1958

Card 2/2

SOV/78-4-7-13/44

5(2)
AUTHORS: Yatsimirskiy, K. B., Naryshkina, Ye. F.

ABSTRACT: The kinetics of the reaction mentioned in the title has already
             been quantitatively investigated, but in the presence of tung-
             state (Ref 2). The said reaction develops according to the
             equation $S_2O_3^{2-} + 4H_2O_2 = 2SO_4^{2-} + 2H_2^+ + 3H_2O$. The reaction rate
             was photometrically measured by the increase of the optical
             density of a suspension of barium sulfate. The results obtained
             are shown by the following diagrams: Figure 1. - Dependence of
             the reaction rate on the concentration of ammonium vanadate.
             Figure 2. - Dependence of the reaction rate on the concentration
             of hydrogen peroxide and thiosulfate. Figure 3. - Dependence of
             the reaction rate on hydrogen ion concentration. Figure 4. -
             Dependence of reaction rate on ionic strength (by the addition

Card 1/3

SOV/78-4-7-13/44

The Kinetics of the Oxidation Reaction of Thiosulphate by Hydrogen Peroxide in the Presence of Vanadate

of NaClO$_4$ or KNO$_3$). For the connection between the reaction rate and the concentration of the reacting substances the following equation is given:

$$\frac{d[SO_4^{2-}]}{dt} = K \cdot c_{NH_4VO_3} \cdot c_{H_2O_2} \cdot c_{S_2O_3^{2-}}, \text{ where } K = 3.8 \cdot 10^7 \text{ mol/l.min.}$$

However, this equation holds only for a certain concentration interval. At very low concentrations of thiosulfate the dependence of the reaction rate on concentration is no longer linear. Table 1 mentions the influence exercised by various foreign ions upon the development of the reaction. By the formation of catalytically inactive complex compounds the reaction is interrupted by the addition of fluorides, citrates, tartrates, phosphates, etc. Univalent cations exercise no noticeable influence upon the development of the reaction. Copper-- and ferrous ions accelerate the reaction by their catalytic effect. There are 5 figures, 1 table, and 5 ref-

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The Kinetics of the Oxidation Reaction of Thiosulphate by Hydrogen Peroxide
in the Presence of Vanadate

SOV/78-4-7-13/44

        erences, 3 of which are Soviet.

ASSOCIATION: Ivanovskiy khimiko-tekhnologicheskiy institut (Ivanovo Chemico-
              technological Institute); Stalingradskiy mekhanicheskiy institut
              (Stalingrad Institute for Mechanics)

SUBMITTED: April 7, 1958

Card 3/3

5(2),5(4)
AUTHORS:

Yatsimirskiy, K. B.,
Drobysheva, O. M., Rigin, V. I.

SOV/75-14-1-11/32

TITLE:

Kinetic Methods of Quantitative Analysis
(Kineticheskiye metody kolichestvennogo analiza).
Communication 5. A Kinetic Method for the Quantitative
Determination of Tantalum (Soobshcheniye 5. Kineticheskiy
metod kolichestvennogo opredeleniya tantala)

PERIODICAL:

Zhurnal analiticheskoy khimii, 1959, Vol 14, Nr 1, pp 60-62
(USSR)

ABSTRACT:

In the present paper the catalytic effect of tantalum (V)
compounds on the oxidation of iodides with hydrogen peroxide
in acid solution is made use of for the elaboration of a
kinetic method for the quantitative determination of small
quantities of tantalum. All the reagents used were carefully
cleaned from heavy metals. The tantalum solution was treated
with certain quantities of potassium iodide and starch
solutions and carefully intermixed. The required quantity of
hydrogen peroxide was then added. After renewed intermixing the
solution was measured in a photo-colorimeter FEK-M at regular

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